

(11) Publication number:

1

Generated Document.

# PATENT ABSTRACTS OF JAPAN

(21) Application number: 10013001

(51) Intl. Cl.: H01M 10/40

(22) Application date: 26.01.98

(30) Priority:

(43) Date of application

publication:

06.08.99

(84) Designated contracting

states:

(71) Applicant: SONY CORP

(72) Inventor: HORIE TAKESHI

NODA KAZUHIRO YAMADA SHINICHIRO

(74) Representative:

(54) NONAQUEOUS ELECTROLYTIC SOLUTION AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING THE SAME

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte solution with superior battery performance and a nonaquepous electrolytic solution battery that restrains vaporization and resolution of the electrolyte solution and simultaneously reduces the possibility of breaking and firing the battery due to a generated gas.

SOLUTION: This nonaqueous electrolyte solution battery is provided with a positive electrode, comprising an oxide or a sulfide that can be doped/dedoped with lithium ions, a negative electrode consisting of a carbon material that can be doped/dedoped with lithium metal, a

lithium alloy, or lithium ions, and a nonaqueous electrolyte solution. The nonaqueous solution is a nonaqueous solution battery comprising a siloxane derivative shown by the formula and at least one kind of lithium metallic salt. In the formula, (a) represents an integer from 1 to 50, (b) represents an integer from 1 to 20, (m) represents an integer from 0 to 40, (n) represents from 0 to 40, R represents a hydrogen element or alkyl each of which can be substituted. However, when b>1, (b) number of Ds may be the same or different.

COPYRIGHT: (C)1999,JPO

$$CH_{3} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3}$$

$$CH_{9} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3}$$

$$CH_{3} \qquad CH_{3}$$

$$CH_{2} - CH_{2} - CH_{2} - O - \{CH_{2} - CH_{2} - O\}_{m} \{CH_{2} - CH_{2} - CH_{2} - CH_{2} - O\}_{m} \{CH_{2} - CH_{2} - CH_{$$

Page 1 of 2

# PATENT ABSTRACTS OF JAPAN

(11)Publication number:

11-214032

(43) Date of publication of application: 06.08.1999

(51)Int.CI.

HO1M 10/40

(21)Application number: 10-013001

(71)Applicant: SONY CORP

(22) Date of filing:

26.01.1998

(72)Inventor: HORIE TAKESHI

NODA KAZUHIRO

YAMADA SHINICHIRO

# (54) NONAQUEOUS ELECTROLYTIC SOLUTION AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING THE SAME

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte solution with superior battery performance and a nonaquepous electrolytic solution battery that restrains vaporization and resolution of the electrolyte solution and simultaneously reduces the possibility of breaking and firing the battery due to a generated gas. SOLUTION: This nonaqueous electrolyte solution battery is provided with a positive electrode, comprising an oxide or a sulfide that can be doped/dedoped with lithium ions, a negative electrode consisting of a carbon material that can be doped/dedoped with lithium metal, a lithium alloy, or lithium ions, and a nonaqueous electrolyte solution. The nonaqueous solution is a nonaqueous solution

battery comprising a siloxane derivative shown by the

formula and at least one kind of lithium metallic salt. In the formula, (a) represents an integer from 1 to 50, (b) represents an integer from 1 to 20, (m) represents an integer from 0 to 40, (n) represents from 0 to 40, R represents a hydrogen element or alkyl each of which can be substituted. However, when b>1, (b) number of Ds may be the same or different.

# **LEGAL STATUS**

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

# The Delphion Integrated View

 Get Now:
 More choices...
 Tools:
 Add to Work File:
 Create new Wo

 View:
 INPADOC
 | Jump to:
 Top
 Image: Create new Wo

**9**Title: JP11214032A2: NONAQUEOUS ELECTROLYTIC SOLUTION AND NONAQUEOUS ELECTROLYTIC SOLUTION BATTERY USING THE:

ଟ Country: JP Japan

**PInventor:** HORIE TAKESHI;

NODA KAZUHIRO; YAMADA SHINICHIRO;

**PAssignee:** SONY CORP

News, Profiles, Stocks and More about this company

Published / Filed: 1999-08-06 / 1998-01-26

**P**Application **JP1998000013001** 

Number: **H01M 10/40**;

**PAbstract:** 

Priority Number: 1998-01-26 JP1998000013001

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte solution with superior battery performance and a nonaquepous electrolytic solution battery that restrains vaporization and resolution of the electrolyte solution and simultaneously reduces the possibility of breaking and firing the battery due to a generated gas.

SOLUTION: This nonaqueous electrolyte solution battery is provided with a positive electrode, comprising an oxide or a sulfide that can be doped/dedoped with lithium ions, a negative electrode consisting of a carbon material that can be doped/dedoped with lithium metal, a lithium alloy, or lithium ions, and a nonaqueous electrolyte solution. The nonaqueous solution is a nonaqueous solution battery comprising a siloxane derivative shown by the formula and at least one kind of lithium metallic salt. In the formula, (a) represents an integer from 1 to 50, (b) represents an integer from 1 to 20, (m) represents an integer from 0 to 40, (n) represents from 0 to 40, R represents a hydrogen element or alkyl each of which can be substituted. However, when b>1, (b) number of Ds may be the same or different.

COPYRIGHT: (C)1999,JPO

None

Get Now: Family Legal Status Report

P Designated

AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

Country:

& Family:

Show 8 known family members



<sup>♀</sup>Other Abstract



CHEMABS 131(08)104524P DERABS C1999-446181







© 1997-2003 Thomson Delphion

Research Subscriptions | Privacy Policy | Terms & Conditions | Site Map | Contac

(19)日本国特許庁 (JP)

(12) 公開特許公報(A)

(11)特許出顧公開番号

特開平11-214032

(43)公開日 平成11年(1999)8月6日

(51) Int.CL\*

教別記号

PI H01M 10/40

A

HO 1 M 10/40

密査部域 未請求 部求項の数9 OL (全 7 頁)

(21)出顧番号	特顧平10-13001	(71)出顧人 000002185	
		ソニー株式会社	
(22)出顧日	平成10年(1998) 1月26日	東京都品川区北品川 6丁目	7番35号
		(72)発明者 堀江 毅	
	٠.	東京都品川区北品川6丁目	17番35号 ソニ
		一株式会社内	•
		(72)発明者 斯田 和宏	
		東京都品川区北岛川 6 丁目	7番35号 ソニ
	•	一株式会社内	
		(72)発明者 山田 心一郎	
		東京都品川区北岛川8丁目	17番35号 ソニ
		一株式会社内	
		(74)代理人 并理士 小池 是 (外2	(名)

#### (54)【発明の名称】 非水電解液及びこれを用いた非水電解液電池

#### (57)【要約】

【課題】 電解液の気化、分解が抑制され、同時にガス 発生による電池の破損、発火の危険性を減じ、かつ電池 性能に優れる非水電解液及び非水電解液電池を提供す る。

【解決手段】 リチウムイオンをドーブ・脱ドーブ可能な酸化物若しくは硫化物からなる正極と、リチウム金属。 リチウム合金、若しくはリチウムイオンをドープ・脱ドープ可能な炭素材料からなる負極と、非水電解液を備える非水電解液電池において、当該非水電解液は、下記の化1にて示されるシロキサン誘導体と少なくとも1種のリチウム金属塩とからなる非水電解液電池。 【化1】

(文中、mix. 1から50の放放を表し、mix. 1から200位並を表し、mix. のから40の放放を表し、mix. 7から400並列を表し、Mix. 水原収子 またなそれぞれ最適されてらよいアルキル社を直す。ただし、b>140 とさは、b日700、は月じても点なっていてもよい。) (2)

特開平11-214032

【特許請求の範囲】

\*を特徴とする非水電解液。

[{t1]

【請求項1】 下記の化1にて示されるシロキサン誘導 体と、少なくとも1種のアルカリ金属塩とからなること\*

く式中。aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 Oから40の整数を表し、n(は、Oから40の整数を表し、Rは、水流原子 またはそれぞれ置換されてもよいアルキル芸を表す。ただし、b>1の ときは、b個のD' は同じでも異なっていてもよい。)

【請求項2】 上記シロキサン誘導体は、温度25℃に おける動粘性率が5000cSt以下であることを特徴 20 とする請求項1記載の非水電解液。

【請求項3】 上記シロキサン誘導体は、平均分子量が 10000以下であることを特徴とする請求項1記載の 非水電解液。

【韻求項4】 上記アルカリ金属塩がリチウム金属塩で あることを特徴とする請求項1記載の非水電解液。

【請求項5】 温度25℃における導電率が0. 1mS ・cm゚゚以上であることを特徴とする請求項1記載の非※

CHa

(式中、Bは、1から50の動散を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水液原子 またはそれぞれ関係されてもよいアルキル基を表す。ただし、b>1の ときは、b個のD' は同じでも異なっていてもよい。)

【請求項7】 上記シロキサン誘導体は、温度25℃に おける動結性率が5000cSt以下であることを特徴 とする請求項6記載の非水電解液電池。

【請求項8】 上記シロキサン誘導体は、平均分子量が 10000以下であることを特徴とする請求項6記載の 非水電解液電池。

【請求項9】

導電率が0.1mS・cm~以上であることを特徴とす る鹽水項 6 記載の非水電解液電池。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、特定の電解液を用 いることにより、短絡時における安全性を向上させ、高 上記非水電解液は、温度25℃における 50 電圧においても優れた電池性能を発揮する非水電解液及

※水電解液。

【請求項6】 リチウムイオンをドーブ・脱ドープ可能 な酸化物若しくは硫化物からなる正極と、リチウム金 屑、リチウム合金、若しくはリチウムイオンをドープ・ 脱ドープ可能な炭素材料からなる負極と、非水電解液と を備える非水電解液電池において、

上記非水電解液は、下記の化2にて示されるシロキサン 誘導体と、少なくとも1種のリチウム金属塩とからなる ことを特徴とする非水電解液電池。

[12]

http://www6.ipdl.jpo.go.jp/tjcontenttrns.ipdl?N0000=21&N0400=image/gif&N0401=/NS...

びこれを用いた非水電解液電池に関するものである。 [0002]

【従来の技術】近年になって、カメラー体型ビデオテー プレコーダ、携帯電話、ラップトップコンピュータ等の 携帯用電気製品が急速に普及しつつある。また、環境保 護の観点からNO、等の排気ガスを空気中に排出しない 電気自動車の開発が社会的課題として取り上げられるよ うになった。このような状況下で、ポータブル電源、及 びクリーンなエネルギー顔としての電池、特に二次電池 についての研究開発が活発に進められている。中でも、 リチウム若しくはリチウムイオン二次電池は、従来の水 系電解液二次電池である鉛電池、ニッケルカドミウム電 池と比較して高いエネルギー密度が得られるため、大き な期待を集めている。

【0003】このリチウム若しくはリチウムイオン電池 の電解液としては、低分子のエチレンカーボネート、ブ ロビレンカーボネートや、炭酸ジエチル等の炭酸エステ ル系非水溶媒に、電解質としてLiPF。等のリチウム 系電解質塩を溶解させた液体状態であるものが、比較的 電導率も高く、電位的にも安定である点から広く用いら れている。

#### [0004]

【発明が解決しようとする課題】ところで、上述した非 水電解液電池は、高性能であるものの、可燃性の有機溶 媒を電解液として用いているため、安全性において問題 がある。例えば、短絡時に急激に大電流が電池内に流れ て発熱し、これによって有機溶媒を含む電解液が気化、 分解をおこし、ガスを発生する問題があった。そして、\*

(式中、aは、1から50の強敵を表し、bは、1から20の整数を表し、mは、 Oから40の整数を表し、nは、Oから40の整数を表し、Rは、木森原子 またはそれぞれ昼後されてもよいアルキル苺を表す。ただし、b>1の ときは、b個のD'は同じでも異なっていてもよい。)

【0010】上記シロキサン誘導体は、温度25℃にお ける助粘性率が50000551以下であることが好まし く、平均分子量が10000以下であることが好まし い。動粘性率及び平均分子量が最適化されることによ り、電解液として使用に耐え得る適正な粘度、混合に適 する溶解性を有する溶媒の合成が可能となる。 【0011】このように、本発明に係る非水電解波は、

\* このガス発生のために、電池の破損、破裂、発火が起こ る可能性があった。これまでは、これらの解決方法とし て、電池内圧の上昇により開裂する安全弁や電流遮断装 置を設ける等の方法がなされていた。

【0005】しかしながら、このような構造機構の改良 方法では、いかなる問題にも対処できるとは限らず、電 池の安全性能を向上させるには、電池材料の根本的な改 苦方法が必要となってきている。

【0006】本発明は、上述のような課題を解決するた 10 めに提案されたものであり、化学的、熱化学的安定性に 優れた非水電解液を提供することを目的とする。そし て、電解液の気化、分解を抑制し、同時にガス発生によ る電池の破損、発火の危険性を減じ、かつ電池性能に優し れた非水電解液電池を提供することを目的とする。 [0007]

【課題を解決するための手段】上記目的を解決するた め、本発明者らは鋭意検討を重ねた結果、電解液材料と して、化学的安定性が高く、難燃性又は低蒸気圧の無機 高分子であるシロキサン誘導体を用いることにより、電 解液の気化、分解を抑制し、同時に電池の破損、発火の 危険性を減じ、優れた電池性能を得ることができること を見いだした。

【0008】すなわち、本発明に係る非水電解液は、下 記の化3にて示されるシロキサン誘導体と、少なくとも 1種のアルカリ金属塩とからなることを特徴とする。 [0009]

[ft3]

化学安定性が高く、鍵燃性又は低蒸気圧の無機高分子で あるシロキサン誘導体を用いていることから、短絡時に おいても電解波の気化、分解を抑制し、電池の破損、発 火の危険性を減じ、高電圧においても優れた電池性能を 有する。

【0012】一方、本発明に係る非水電解液電池は、リ 50 チウムイオンをドープ・脱ドープ可能な酸化物苦しくは

硫化物からなる正極と、リチウム金属、リチウム合金、 若しくはリチウムイオンをドープ・脱ドープ可能な炭素 材料からなる負極とを備える。そして、本発明に係る非 水電解液電池は、下記の化4にて示されるシロキサン請※

\*導体と、少なくとも1種のリチウム金属塩とからなる非 水電解液を備えることを特徴とする。

[0013] [1:4]

ÇH3

(4)

(式中、aは、1から50の整数を表し、bは、tから20の整数を表し、mは... 0から40の整数を表し、nは、0から40の整数を表し、Rは、水流原子 またはそれぞれ登換されてもよいアルキル器を表す。ただし、b>1の ときは、b個のD' は同じでも異なっていてもよい。)

【0014】上記シロキサン誘導体は、温度25℃にお 20%も優れた電池性能を有する。 ける助粘性率が5000cSt以下であることが好まし

く、平均分子量が10000以下であることが好まし い。助粘性率及び平均分子量が最適化されることによ

り、電解液として使用に耐え得る適正な粘度、混合に適 する溶解性を有する溶媒の合成が可能となる。

【0015】このように、本発明に係る非水電解液電池 は、電解液として、化学安定性が高く、難燃性又は低蒸 気圧の無機高分子であるシロキサン誘導体を用いてなる ことから、短絡時においても電解液の気化、分解を抑制 し、電池の破損、発火の危険性を減じ、高電圧において※30

[0016]

【発明の実施の形態】以下、本発明に係る非水電解液及 びこれを用いた非水電解液電池について詳細に説明す る.

【0017】本発明に係る非水電解液は、下記の化5に て示されるシロキサン誘導体と、少なくとも1種のアル カリ金屑塩とからなることを特徴とする。

[0018]

[ft5]

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水源原子 またはそれぞれ階換されてもよいアルキル基を表す。ただし、b>1の ときは、6月の0′は同じでも異なっていてもよい。)

【0019】上記シロキサン誘導体は、硅素と酸素の鎖 状結合を基本骨骼にもち、硅素に1個の有機基である側 鎖基が付加された鎖状型シロキサン誘導体であり、化学 的安定性が高く、難燃性若しくは低蒸気圧であるために 熱化学的安定性にも優れる無機商分子である。

【0020】さらに、このシロキサン誘導体には、粘度 が比較的低い溶液状であり、かつアルカリ金属塩を溶解 し得る構造が求められる。すなわら、シロキサン誘導体 は、温度25℃における動粘性率が5000cSt (セ 50 ンチストークス)以下であり、平均分子量が10000

以下であることが求められる。

【0021】さらに、電解液としては、温度25℃にお ける導電率がり、1mS・cm<sup>-1</sup>以上であることがより

【0022】電解液として使用に耐え得る適正な粘度、 混合に過する溶解性は、化5で示されるD, D'の側鎖 基を適度に選択することにより可能となる。 化5 で示さ れるD、の側鎖基は、エーテル結合を含むことが有利で ある。また、aは1~50であり、bは1~20であ り、aとりの和は、1~40であることがより好まし い。なお、D、D、、及び置換基R中の水素は、ファ 素、ホウ素等のハロゲン元素で置き換えられていてもよ

【0023】一方、上述したシロキサン誘導体に溶解さ せるアルカリ金属塩には、リチウム、ナトリウム、アル ミニウム等の軽金属の塩を使用することができ、当該非 水電解液を使用する電池の種類に応じて便宜定めること

【0024】例えば、リチウム若しくはリチウムイオン 二次電池を構成する場合には、LiBF。 LICI O. Lipf. Liasf. CF.SO.Li. (C F, SO, ), NL 1. C, F, SO, Li. CF, CO, L 1. (CF,CO,),NL1, C,F,SO,L1. C,F ,, SO, Li, (C, F, SO,), NL, (C, F, S  $O_2$ ) (CF<sub>2</sub>SO<sub>2</sub>) NL<sub>1</sub>, (FSO<sub>2</sub>C<sub>4</sub>F<sub>4</sub>) (CF 150,) NLi. ((CF,), CHOSO,), NLi.  $(CF_{2}SO_{2})_{1}CLi_{1}(C_{1}F_{2}(CF_{1})_{2}-3,$ 5) BLi、LICF: LIAICI,等のリチウム 塩を使用することができる。

【0025】このように、上述したシロキサン誘導体と アルカリ金属塩を含有する非水電解液は、化学的安定 性、熱化学的安定性に優れるシロキサン誘導体を溶媒と して用いてなることから、短絡時に急激に大電流が流れ た場合においても、電解波の気化、分解が抑制される。 したがって、この非水電解液を用いた非水電解液電池 は、短絡時の電池の急速な破損や発火の危険性が減じら れ、安全性が向上し、かつ高電圧においても優れた電池 性能を発揮することができる。

【0026】以上、上述した非水電解液は、リチウムを ドープ・脱ドープ可能な酸化物若しくは硫化物からなる 40 正極と、リチウム金属、リチウム台金、若しくはリチウ ムイオンをドープ・脱ドープ可能な炭素質材料からなる 負極とを備えた非水電解液二次電池の電解液として用い て好酒である。

【0027】例えば、リチウム二次電池を構成する場 台、正極活物質としては、TIS,, MoS,, NbSe ,、V,O,等のリチウムを含有しない金屑硫化物着しく は酸化物、又はリチウムを含有するリチウム複合酸化物 を使用することができる。

成するためには、Li、MO、(式中、Mは1種類以上の 遷移金鷹が好ましく、0. 05≤x≤1. 10であ る。) を主体とするリチウム複合酸化物が好ましく用い られる。リチウム複合酸化物としては、具体的に、 Lェ CoO, LINIO, Li, Ni, Co, ,, O, (式中、 x. yは電池の放電状態によって異なり、通常O<x< 1. 0. 7 < y ≤ 1 である。)、L i Mn, O,等が挙げ られる。

【0029】このようなリチウム複合酸化物は、リチウ 10 ムの炭酸塩、硝酸塩、酸化物、若しくは水酸化物と、コ バルト、マンガン、若しくはニッケル等の炭酸塩、硝酸 塩、酸化物、若しくは水酸化物とを所望の組成に応じて 粉砕混合し、酸素雰囲気で600~1000°Cの温度範 囲で焼成することにより調整することができる。

【0030】また、負極としては、リチウム、Li-A 1合金等のリチウム合金。 若しくはリチウムイオンをド ープ・脱ドープ可能な炭素材料等を使用することができ る。炭素材料としては、所定の温度、雰囲気にて調整し たものが用いられる。この原料としては、例えば、熱分 20 解炭素類、コークス類(石油コークス、ピッチコークス 等)、人造黒鉛類、天然黒鉛類、カーボンブラック(ア セチレンブラック等)、ガラス状炭素類、有機高分子材 料焼成体(有機高分子材料を不活性ガス気流中、あるい は真空中で500℃以上の適当な温度で焼成したも の) 炭素繊維等を使用することができる。

【0031】さらに、非水電解液の溶媒としては、上述 したシロキサン誘導体の1種単独でも使用することがで きるが、従来公知の他の溶媒と併用して使用してもよ い。他の溶媒としては、例えば、プロビレンカーボネー ト、エチレンカーボネート、ジエチルカーボネート、メ チルエチルカーボネート、1、2-ジメトキシエタン、 1、2-ジェトキシエタン、ァープチロラクトン、テト **ラヒドロフラン、1、3 – ジオキソラン、ジブロビルカ** ーポネート、ジエチルエーテル、スルホラン、メチルス ルホラン、アセトニトリル、プロビルニトリル、アニソ ール、酢酸エステル、プロビオン酸エステル、2-メチ ルテトラヒドロフラン等を使用することができ、2種類 以上混合して使用してもよい。

【0032】上述した正極及び負極の両極の接触による 電流の短絡等を防ぐためのセパレータとしては、両極の 接触を確実に防止することができ、かつ電解液を通した り含んだりすることができる材料、例えばポリテトラフ ルオロエチレン、ポリプロビレン、ポリエチレン等の台 成樹脂製の不線布、多孔質セラミックフィルム、若しく は多孔質薄膜フィルム等を使用することができる。

【0033】このように、電解液として、化学的安定性 が高く、難燃性、若しくは低蒸気圧の無機高分子のシロ キサン誘導体を用いた非水電解液電池においては、電解 液の気化、分解が抑制され、同時に発火、引火の危険性 【0028】特に、高エネルギー密度を有する電池を構 50 が減じられ、かつ高電圧においても電池性能に優れたも

特開平11-214032

10

のとなる。

【0034】なお、本発明の電池のその他の構成部材としては、通常使用されているものを支障なく使用することができる。また、電池の形態は特に制限されず、コインタイプ、ボタンタイプ、ペーパータイプ、角型又はスパイラル構造の微型電池等、電池の形態は関われない。【0035】

【実施例】以下、本発明を実施例により具体的に説明するが、本発明はこれに限定されるものではない。

【0036】実施例1

下記の化6~化8にて示されるシロキサン誘導体(1)

~(3)にリチウム塩の濃度を変えてそれぞれ添加し、\*

\*た。そして、これらをそれぞれ厚さり、145cm、面積り、7854cm\*のステンレス板にはさみ、ED加する正弦波交流電圧を記号法(搜索表示)で表現した、いわゆるコール・コール(Cole-Cole)プロットから導電率を求めた。この結果を表1に示す。
【0037】なお、各々の25℃での動粘性率は、化6で示されるシロキサン誘導体(1)が100cSt、化7で示されるシロキサン誘導体(2)が1600cSt、化8で示されるシロキサン誘導体(3)が400c

10 Stであった。 【0038】

[(16)

(6)

・・根遊式 (1)

・・構造式 (2)

(Bu= ---CH2-CH2-CH2-CH3)

[0040]

・・・横造式 (3)

[0041]

【表1】

【0042】表1の結果から、化6~化8で示されるシロキサン誘導体は、いずれも電池に使用できる導電性をもつことがわかる。また、助結性率の異なるシロキサン誘導体(1)~(3)では、より低い動結性率を持つシロキサン誘導体(1)を用いた方がより高い導電率を得 20 ちれることがわかる。

#### 【0043】実施例2

先の化6及び化7で示されるシロキサン誘導体(1) (2)のサイクリック・ボルタモグラムを測定して酸化 安定性を調べた。測定は、3電極製の電気化学セルを使 用し、作用極にニッケル電極(直径:0.5 mm)、対 極と参照極にリチウム金属を使用した。そして、100 ルA・c m<sup>-1</sup>の酸化電流が発生するまでの電位を安定な 電位の範囲とした。その結果、サンブル2の酸化安定電 位は、5.8 V、サンブル6の酸化安定電位は、6.0 Vとなった。

【0044】この結果から、シロキサン誘導体は、高電圧においても優れた電池性能を発揮できることがわかる。

#### \*【0045】実施例3

正極にLICOO、負極に炭素材料、電解液に化6にて示されるシロキサン誘導体(1)用いたコインセルを作製して、充放電試験を行った。上限電圧:4.2V、下限電圧:3.0V、放電電流:100μAの条件で20サイクルまで充放電を繰り返した。その時の充放電試験を図1に示す。

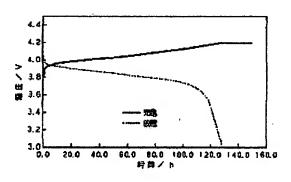
【0046】図1の結果から、シロキサン誘導体(1)は、電池として優れた電池性能を有することがわかる。 【0047】

【発明の効果】以上の説明からも明らかなように、本発明によれば、特定のシロキサン誘導体を電解液として用いてなることから、化学的、熱化学的安定性に優れた非水電解液を得ることができ、安全性に優れ、高電圧にも優れた電池性能を有する非水電解液電池を得ることができる。

#### 【図面の簡単な説明】

【図1】本実施例の非水電解液電池の充放電曲線を示す 特性図である。





シロキサン電池の充刻型的絵

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## **CLAIMS**

## [Claim(s)]

[Claim 1] Nonaqueous electrolyte characterized by the bird clapper from the siloxane derivative shown by following \*\* 1, and at least one sort of alkali-metal salts.

D= 
$$-\frac{\zeta_{13}}{\zeta_{13}}$$
  
CH<sub>3</sub>  
CH<sub>3</sub>  
D=  $-\frac{\zeta_{13}}{\zeta_{13}}$   
CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O- $\frac{\zeta_{12}}{\zeta_{13}}$   
CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O- $\frac{\zeta_{13}}{\zeta_{13}}$ 

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子 またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1の ときは、b個のD'は同じでも異なっていてもよい。)

[Claim 2] The above-mentioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C being 5000 or less cSts.

[Claim 3] The above-mentioned siloxane derivative is nonaqueous electrolyte according to claim 1 characterized by average molecular weight being 10000 or less.

[Claim 4] Nonaqueous electrolyte according to claim 1 characterized by the above-mentioned alkalimetal salt being a lithium metal salt.

[Claim 5] Nonaqueous electrolyte according to claim 1 characterized by the conductivity in the temperature of 25 degrees C being -one or more 0.1 mS-cm.

[Claim 6] It is the nonaqueous electrolyte cell characterized by the bird clapper from the siloxane derivative in which the above-mentioned nonaqueous electrolyte is shown by following \*\* 2 in a nonaqueous electrolyte cell equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a \*\* dope of a lithium ion are possible, the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a \*\* dope of a lithium ion are possible, and nonaqueous electrolyte, and at least one sort of lithium metal salts. [Formula 2]

D= 
$$-Si-O$$
  
.  $CH_3$   
 $CH_3$   
D=  $-Si-O$   
 $CH_2-CH_2-CH_2-O$   
 $CH_2-CH_2-CH_2-O$   
 $CH_2-CH_2-O$   
 $CH_3-CH_3-O$ 

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子 またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1の ときは、b個のD'は同じでも異なっていてもよい。)

[Claim 7] The above-mentioned siloxane derivative is a nonaqueous electrolyte cell according to claim 6 characterized by the coefficient of kinematic viscosity in the temperature of 25 degrees C being 5000 or less cSts.

[Claim 8] The above-mentioned siloxane derivative is a nonaqueous electrolyte cell according to claim 6 characterized by average molecular weight being 10000 or less.

[Claim 9] The above-mentioned nonaqueous electrolyte is a nonaqueous electrolyte cell according to claim 6 characterized by the conductivity in the temperature of 25 degrees C being -one or more 0.1 mS-cm.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] By using the specific electrolytic solution, this invention raises the safety at the time of a short circuit, and relates to the nonaqueous electrolyte cell using the nonaqueous electrolyte and this which demonstrate the cell performance which was excellent also in the high voltage.

[0002]

[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, and a laptop computer, are spreading quickly. Moreover, development of the electric vehicle which does not discharge exhaust gas, such as NOx, in air came to be taken up from a viewpoint of environmental protection as a social technical problem. Under such a situation, the research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are furthered actively. Especially, since a high energy density is obtained as compared with the lead cell and nickel-cadmium battery which are the conventional drainage system electrolytic-solution rechargeable battery, the lithium or the rechargeable lithium-ion battery attracts great expectation. [0003] As the electrolytic solution of this lithium or a lithium ion battery, also as for electric conductivity, what is in the liquid state where the lithium system electrolyte salt of LiPF6 grade was dissolved as an electrolyte is comparatively high to low-molecular ethylene carbonate, propylene carbonate, and carbonate system non-aqueous solvents, such as diethyl carbonate, and is widely used for them from the point stable also in potential.

[Problem(s) to be Solved by the Invention] By the way, although the nonaqueous electrolyte cell mentioned above is highly efficient, since the inflammable organic solvent is used for it as the electrolytic solution, it has a problem in safety. For example, the high current flowed and generated heat in the cell rapidly at the time of a short circuit, the electrolytic solution which contains an organic solvent by this caused evaporation and decomposition, and there was a problem which generates gas. And breakage of a cell, rupture, and ignition may have taken place for this generation of gas. Methods, such as preparing the relief valve and current interrupting device which cleave by elevation of cell internal pressure as these solution methods until now, were made.

[0005] However, by such improvement method of a structure mechanism, in order not to restrict that any problems can be coped with but to raise the safe performance of a cell, the fundamental improvement method of cell material is needed.

[0006] this invention is proposed in order to solve the above technical problems, and it aims at offering nonaqueous electrolyte excellent in chemical and thermochemical stability. And it aims at offering the nonaqueous electrolyte cell which suppressed evaporation of the electrolytic solution, and decomposition, and reduced breakage of the cell by the generation of gas, and the danger of ignition simultaneously, and was excellent in the cell performance.

[0007]

[Means for Solving the Problem] In order to solve the above-mentioned purpose, this invention persons had high chemical stability as an electrolytic-solution material, as a result of repeating examination wholeheartedly, and by using the siloxane derivative which is the inorganic polymer of http://www4.ipdl.jpo.go.jp/cgi-bin/tran\_web\_cgi\_ejje 6/4/2003

fire-resistant or low vapor pressure, evaporation of the electrolytic solution and decomposition were suppressed, breakage of a cell and the danger of ignition were reduced simultaneously, and it found out that the outstanding cell performance could be obtained.

[0008] That is, the nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following \*\* 3, and at least one sort of alkali-metal salts.

[0009]

$$D = \frac{CH_3}{CH_3}$$

$$D' = \frac{CH_3}{CH_2 - CH_2 - CH$$

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[0010] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ]. [0011] Thus, the nonaqueous electrolyte concerning this invention has high chemistry stability, since the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure is used for it, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage.

[0012] On the other hand, the nonaqueous electrolyte cell concerning this invention is equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a \*\* dope of a lithium ion are possible, and the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a \*\* dope of a lithium ion are possible. And the nonaqueous electrolyte cell concerning this invention is characterized by having nonaqueous electrolyte which consists of a siloxane derivative shown by following \*\* 4, and at least one sort of lithium metal salts. [0013]

CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O-+CH<sub>2</sub>-CH<sub>2</sub>-O-+R http://www4.ipdl.jpo.go.jp/cgi-bin/tran\_web\_cgi\_ejje (式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[0014] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ]. [0015] Thus, as the electrolytic solution, the nonaqueous electrolyte cell concerning this invention has high chemistry stability, using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage from a bird clapper. [0016]

[Embodiments of the Invention] Hereafter, the nonaqueous electrolyte cell using the nonaqueous electrolyte and this concerning this invention is explained in detail.

[0017] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following \*\* 5, and at least one sort of alkali-metal salts.
[0018]

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子 またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1の ときは、b個のD'は同じでも異なっていてもよい。)

[0019] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic skeleton, and the side chain radical which is a univalent organic machine was added to the silicon, its chemical stability is high, and since the above-mentioned siloxane derivative is fire retardancy or low vapor pressure, it is an inorganic polymer which is excellent also in thermochemical stability.

[0020] Furthermore, viscosity is a low solution-like comparatively, and this siloxane derivative is asked for the structure where an alkali-metal salt may be dissolved. That is, coefficients of kinematic viscosity [ in / the temperature of 25 degrees C / in a siloxane derivative ] are below 5000cSt(s) (centistokes), and it is called for that average molecular weight is 10000 or less.

[0021] Furthermore, it is more desirable that the conductivity in the temperature of 25 degrees C is one or more 0.1 mS-cm as the electrolytic solution.

[0022] The proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture become possible by choosing moderately the side chain radical of D shown by \*\*

5, and D'. As for the side chain radical of D' shown by \*\* 5, it is advantageous to include ether linkage. Moreover, a is 1-50, b is 1-20 and, as for the sum of a and b, it is more desirable that it is 1-40. In addition, the hydrogen in D, D', and Substituent R may be replaced by halogens, such as a fluorine and boron.

[0023] According to the kind of cell which can use the salt of light metals, such as a lithium, sodium, and aluminum, and uses the nonaqueous electrolyte concerned, it can set to the alkali-metal salt dissolved in the siloxane derivative mentioned above on the other hand expedient.

[0024] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4)

NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2-5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)

[0025] Thus, when a high current flows rapidly from a bird clapper at the time of a short circuit, using as a solvent the siloxane derivative the nonaqueous electrolyte containing the siloxane derivative mentioned above and an alkali-metal salt excels [derivative] in chemical stability and thermochemical stability, evaporation of the electrolytic solution and decomposition are suppressed. Therefore, the cell performance which the danger of rapid breakage of the cell at the time of a short circuit or ignition was reduced, and safety of the nonaqueous electrolyte cell using this nonaqueous electrolyte improved, and was excellent also in the high voltage can be demonstrated.

[0026] As mentioned above, the nonaqueous electrolyte mentioned above uses as the electrolytic solution of the nonaqueous electrolyte rechargeable bettery equipped with the positive electrolyte.

solution of the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a \*\* dope of a lithium are possible, and the negative electrode which consists of carbonaceous material in which a dope and a \*\* dope of a lithium metal, a lithium alloy, or a lithium ion are possible and is suitable.

[0027] For example, when it constitutes a lithium secondary battery, as a positive active material, the metallic sulfide which does not contain the lithium of TiS2, MoS2, NbSe2, and V2O5 grade, an oxide, or the lithium multiple oxide containing a lithium can be used.

[0028] In order to constitute the cell which has high-energy density especially, the lithium multiple

oxide which makes a subject LixMO2 (one or more kinds of transition metals of M are desirable, and it is 0.05<=x<=1.10 among a formula.) is used preferably. As a lithium multiple oxide, LiCoO2, LiNiO2, LixNiyCo1-yO2 (among a formula, x and y change with electric discharge states of a cell, and are usually 0< x<1 and 0.7< y<=1.), and LiMn2O4 grade are mentioned concretely. [0029] According to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, an oxide or a hydroxide, trituration mixture of such a lithium multiple oxide can be carried out, and it can be adjusted by calcinating by the 600-1000-degree C temperature requirement in oxygen atmosphere. [0030] Moreover, as a negative electrode, lithium alloys, such as a lithium and an Li-aluminum alloy.

[0030] Moreover, as a negative electrode, lithium alloys, such as a lithium and an Li-aluminum alloy, or the carbon material in which a dope and a \*\* dope of a lithium ion are possible can be used. What was adjusted in predetermined temperature and atmosphere as a carbon material is used. As this raw material, pyrolytic carbons, corks, artificial graphites (petroleum coke, pitch coke, etc.), natural graphites, carbon black (acetylene black etc.), glassy carbons, an organic polymeric-materials baking object (what calcinated organic polymeric materials at the suitable temperature of 500 degrees C or more in the inert gas air current or the vacuum), a carbon fiber, etc. can be used, for example. [0031] Furthermore, although it can use the one-sort independent which is the siloxane derivative mentioned above as a solvent of nonaqueous electrolyte, you may use it conventionally, using together with other well-known solvents. As other solvents, propylene carbonate, ethylene carbonate, diethyl carbonate, methylethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, gammabutyrolactone, a tetrahydrofuran, 1, 3-dioxolane, dipropyl carbonate, diethylether, a sulfolane, a methyl sulfolane, an acetonitrile, propyl nitril, an anisole, acetic ester, propionic-acid ester, 2-methyl tetrahydrofuran, etc. can be used, and two or more kinds may use it, for example, mixing. [0032] A nonwoven fabric, a porosity ceramic film, or a porosity thin film film made of synthetic

resin, such as the material which can prevent contact of two poles certainly, and, and can contain or can be carried out as separator for preventing the short circuit of the current by contact of the positive

electrode mentioned above and the two poles of a negative electrode etc., for example, a polytetrafluoroethylene, polypropylene, and polyethylene, etc. can be used. [ letting the electrolytic solution pass ]

[0033] Thus, as the electrolytic solution, chemical stability is high and it becomes what evaporation of the electrolytic solution and decomposition were suppressed, and the danger of ignition and ignition was simultaneously reduced, and was excellent in the cell performance also in the high voltage in the nonaqueous electrolyte cell using the siloxane derivative of the inorganic polymer of fire-resistant or low vapor pressure.

[0034] In addition, as a composition member of others of the cell of this invention, what is usually used can be used convenient. Moreover, especially the gestalt of a cell is not restricted and the gestalt of cells, such as a telescopic cell of a coin type, a button type, a paper type, a square shape, or spiral structure, is not asked.

[0035]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to this.

[0036] The concentration of lithium salt was changed into siloxane derivative (1) - (3) shown by \*\* 6 of the example 1 following --izing 8, and it added, respectively. And these were inserted into the stainless steel board of 2 the thickness of 0.145cm, and an area of 0.7854cm, respectively, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). This result is shown in Table 1.

[0037] In addition, the siloxane derivatives (3) in which the siloxane derivative (2) in which the siloxane derivative (1) in which the coefficient of kinematic viscosity in each 25 degrees C is shown by \*\* 6 is shown by 100cSt(s) and \*\* 7 is shown by 1600cSt(s) and \*\* 8 were 400cSt(s). [0038]

[Formula 6]  

$$CH_3$$
  $CH_3$   $C$ 

・構造式 (1)

[0040] [Formula 8]

• • - 構造式(3)

[0041]

[ I able I]				
サンプルNo.	シロキサン誘導体	Li塩の種類	重量モル濃度(m)	導電率(25℃)[mS·cm <sup>-1</sup> ]
サンプル1	構造式(1)	(CF3SO2)2NLi	0.5	2.20x10 <sup>-1</sup>
サンプル2	構造式(1)	(CF3SO2)2NLI	1.0	2.25x10 <sup>-1</sup>
サンプル3	構造式(1)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	0.5	1.20x10 <sup>-1</sup>
サンプル4	構造式(1)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	1.0	1.26x10 <sup>-1</sup>
サンプル5	構造式 (2)	(CF3SO2)2NLi	0.5	2.09×10 <sup>-2</sup>
サンブル6	構造式(2)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLi	1.0	4.05×10 <sup>-2</sup>
サンプル7	構造式(2)	(CF3SO2)3CLI	0.5	3.64×10 <sup>-2</sup>
サンブル8	構造式 (2)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	1.0	3.80x10 <sup>-2</sup>
サンプル9	構造式(3)	(CF3SO2)2NLi	0.5	4.62×10 <sup>-2</sup>
サンブル10	構造式 (3)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLi	1.0	4.80x10 <sup>-2</sup>
サンブル11	構造式(3)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	0.5	2.75x10 <sup>-2</sup>
サンプル12	構造式 (3)	(CF3SO2)3CLI	1.0	2.88x10 <sup>-2</sup>

[0042] The result of Table 1 shows that each siloxane derivative shown by \*\* 6 --izing 8 has the conductivity which can be used for a cell. Moreover, in siloxane derivative (1) - (3) from which a coefficient of kinematic viscosity differs, it turns out that conductivity with higher using the siloxane derivative (1) which has a low coefficient of kinematic viscosity more can be obtained. [0043] The cyclic voltamogram of the siloxane derivative (1) shown by \*\* 6 and \*\* 7 of the example 2 point and (2) was measured, and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, and used the lithium metal for the operation pole on the nickel electrode (diameter: 0.5mm), the counter electrode, and the reference pole. And potential until the oxidation current of 100microA-cm -2 occurs was made into the range of stable potential. Consequently, 5.8V and the oxidization stable potential of a sample 6 were set to 6.0V by the oxidization stable potential of a sample 2.

[0044] This result shows that a siloxane derivative can demonstrate the cell performance which was excellent also in the high voltage.

[0045] The coin cell siloxane derivative [ which is shown to LiCoO2 and a negative electrode by the carbon material, and is shown in the electrolytic solution by \*\* 6 ] (1) Used for example 3 positive electrode was produced, and the charge and discharge test was performed. Upper-limit voltage: Charge and discharge were repeated up to 20 cycles on condition that 4.2V, minimum voltage:3.0V, and discharge current:100microA. The charge and discharge test at that time is shown in drawing 1. [0046] The result of drawing 1 shows that a siloxane derivative (1) has the cell performance which was excellent as a cell.

#### [0047]

[Effect of the Invention] According to this invention, the nonaqueous electrolyte cell which has the cell performance which could obtain nonaqueous electrolyte excellent in chemical and thermochemical stability, was excellent in safety, and was excellent also in the high voltage from the bird clapper can be obtained, using a specific siloxane derivative as the electrolytic solution so that clearly also from the above explanation.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## **TECHNICAL FIELD**

[The technical field to which invention belongs] By using the specific electrolytic solution, this invention raises the safety at the time of a short circuit, and relates to the nonaqueous electrolyte cell using the nonaqueous electrolyte and this which demonstrate the cell performance which was excellent also in the high voltage.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### PRIOR ART

[Description of the Prior Art] Recent years come and portable electrical-and-electric-equipment products, such as a camera one apparatus video tape recorder, a cellular phone, and a laptop computer, are spreading quickly. Moreover, development of the electric vehicle which does not discharge exhaust gas, such as NOx, in air came to be taken up from a viewpoint of environmental protection as a social technical problem. Under such a situation, the research and development about the cell as a portable power supply and a clean energy source, especially a rechargeable battery are furthered actively. Especially, since a high energy density is obtained as compared with the lead cell and nickel-cadmium battery which are the conventional drainage system electrolytic-solution rechargeable battery, the lithium or the rechargeable lithium-ion battery attracts great expectation. [0003] As the electrolytic solution of this lithium or a lithium ion battery, also as for electric conductivity, what is in the liquid state where the lithium system electrolyte salt of LiPF6 grade was dissolved as an electrolyte is comparatively high to low-molecular ethylene carbonate, propylene carbonate, and carbonate system non-aqueous solvents, such as diethyl carbonate, and is widely used for them from the point stable also in potential.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, the nonaqueous electrolyte cell which has the cell performance which could obtain nonaqueous electrolyte excellent in chemical and thermochemical stability, was excellent in safety, and was excellent also in the high voltage from the bird clapper can be obtained, using a specific siloxane derivative as the electrolytic solution so that clearly also from the above explanation.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, although the nonaqueous electrolyte cell mentioned above is highly efficient, since the inflammable organic solvent is used for it as the electrolytic solution, it has a problem in safety. For example, the high current flowed and generated heat in the cell rapidly at the time of a short circuit, the electrolytic solution which contains an organic solvent by this caused evaporation and decomposition, and there was a problem which generates gas. And breakage of a cell, a burst, and ignition may have taken place for this generation of gas. Methods, such as preparing the relief valve and current interrupting device which cleave by the rise of cell internal pressure as these solution methods until now, were made.

[0005] However, by such improvement method of a structure mechanism, in order not to restrict that any problems can be coped with but to raise the safe performance of a cell, the fundamental improvement method of cell material is needed.

[0006] this invention is proposed in order to solve the above technical problems, and it aims at offering nonaqueous electrolyte excellent in chemical and thermochemical stability. And it aims at offering the nonaqueous electrolyte cell which suppressed evaporation of the electrolytic solution, and decomposition, and reduced breakage of the cell by the generation of gas, and the danger of ignition simultaneously, and was excellent in the cell performance.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2. \*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **MEANS**

[Means for Solving the Problem] In order to solve the above-mentioned purpose, this invention persons had high chemical stability as an electrolytic-solution material, as a result of repeating examination wholeheartedly, and by using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, evaporation of the electrolytic solution and decomposition were suppressed, breakage of a cell and the danger of ignition were reduced simultaneously, and it found out that the outstanding cell performance could be obtained.

[0008] That is, the nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following \*\* 3, and at least one sort of alkali-metal salts.

[0009]

D= 
$$\frac{\sqrt{113}}{\text{CH}_3}$$
  
CH<sub>3</sub>  
D'=  $\frac{\sqrt{113}}{\text{CH}_3}$   
D'=  $\frac{\sqrt{113}}{\text{CH}_3}$   
CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O- $\frac{\sqrt{112}}{\text{CH}_2}$   
CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-O- $\frac{\sqrt{112}}{\text{CH}_3}$ 

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子 またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1の ときは、b個のD'は同じでも異なっていてもよい。)

[0010] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ]. [0011] Thus, the nonaqueous electrolyte concerning this invention has high chemistry stability, since the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure is used for it, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage.

[0012] On the other hand, the nonaqueous electrolyte cell concerning this invention is equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a \*\* dope of a lithium ion are possible, and the negative electrode which consists of a lithium metal, a lithium alloy, or a carbon material in which a dope and a \*\* dope of a lithium ion are possible. And the nonaqueous

electrolyte cell concerning this invention is characterized by having nonaqueous electrolyte which consists of a siloxane derivative shown by following \*\* 4, and at least one sort of lithium metal salts. [0013]

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1のときは、b個のD'は同じでも異なっていてもよい。)

[0014] As for the above-mentioned siloxane derivative, it is desirable that the coefficient of kinematic viscosity in the temperature of 25 degrees C is 5000 or less cSts, and it is desirable that average molecular weight is 10000 or less. By optimizing a coefficient of kinematic viscosity and average molecular weight, it becomes compoundable [ the solvent which has the proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture ]. [0015] Thus, as the electrolytic solution, the nonaqueous electrolyte cell concerning this invention has high chemistry stability, using the siloxane derivative which is the inorganic polymer of fire-resistant or low vapor pressure, it suppresses evaporation of the electrolytic solution, and decomposition at the time of a short circuit, reduces breakage of a cell, and the danger of ignition, and has the cell performance which was excellent also in the high voltage from a bird clapper. [0016]

[Embodiments of the Invention] Hereafter, the nonaqueous electrolyte cell using the nonaqueous electrolyte and this concerning this invention is explained in detail.

[0017] The nonaqueous electrolyte concerning this invention is characterized by the bird clapper from the siloxane derivative shown by following \*\* 5, and at least one sort of alkali-metal salts.
[0018]

[Formula 5]

$$CH_3$$
 $CH_3$ 
 $CH_3$ 

(式中、aは、1から50の整数を表し、bは、1から20の整数を表し、mは、 0から40の整数を表し、nは、0から40の整数を表し、Rは、水素原子 またはそれぞれ置換されてもよいアルキル基を表す。ただし、b>1の ときは、h個のD'は同じでも異なっていてもよい。) http://www4.ipdl.jpo.go.jp/cgi-bin/tran\_web\_cgi\_ejje [0019] It is the shape type siloxane derivative of a chain with which it had the chain combination of a silicon and oxygen in the basic frame, and the side chain radical which is a univalent organic machine was added to the silicon, its chemical stability is high, and since the above-mentioned siloxane derivative is fire retardancy or low vapor pressure, it is an inorganic polymer which is excellent also in thermochemical stability.

[0020] Furthermore, the structure where it has the shape of a solution with comparatively low viscosity, and an alkali-metal salt may be dissolved in this siloxane derivative is searched for. That is, coefficients of kinematic viscosity [ in / the temperature of 25 degrees C / in a siloxane derivative ] are below 5000cSt(s) (centistokes), and it is called for that average molecular weight is 10000 or less.

[0021] Furthermore, it is more desirable that the conductivity in the temperature of 25 degrees C is one or more 0.1 mS-cm as the electrolytic solution.

[0022] The proper viscosity which can be equal to use as the electrolytic solution, and the solubility suitable for mixture become possible by choosing moderately the side chain radical of D shown by \*\* 5, and D'. As for the side chain radical of D' shown by \*\* 5, it is advantageous to include ether linkage. Moreover, a is 1-50, b is 1-20 and, as for the sum of a and b, it is more desirable that it is 1-40. In addition, the hydrogen in D, D', and Substituent R may be replaced by halogens, such as a fluorine and boron.

[0023] According to the kind of cell which can use the salt of light metals, such as a lithium, sodium, and aluminum, and uses the nonaqueous electrolyte concerned, it can set to the alkali-metal salt dissolved in the siloxane derivative mentioned above on the other hand expedient.

[0024] for example, in constituting a lithium or a rechargeable lithium-ion battery LiBF4, LiClO4, LiPF6, LiAsF6, CF3SO3Li, 2NLi, C4F9SO3Li, CF3CO2Li, (CF3SO2) 2NLi, C6F5SO3Li, C8F17SO3Li, (CF3CO2) It NLi(s) and NLi(s) (CF(C4F9SO2)3SO2). (C2F5SO2) 2 -- (FSO2C6F4) NLi, 2(2(CF3) CHOSO2) NLi, 3(CF3SO2) CLi, and 4 (3 C6F3(CF3)2-5) -- the lithium salt of BLi, LiCF3, and LiAlCl4 grade can be used (CF3SO2)

[0025] Thus, when a high current flows rapidly from a bird clapper at the time of a short circuit, using as a solvent the siloxane derivative the nonaqueous electrolyte containing the siloxane derivative mentioned above and an alkali-metal salt excels [derivative] in chemical stability and thermochemical stability, evaporation of the electrolytic solution and decomposition are suppressed. Therefore, the cell performance which the danger of rapid breakage of the cell at the time of a short circuit or ignition was reduced, and safety of the nonaqueous electrolyte cell using this nonaqueous electrolyte improved, and was excellent also in the high voltage can be demonstrated.

[0026] As mentioned above, the nonaqueous electrolyte mentioned above uses as the electrolytic solution of the nonaqueous electrolyte rechargeable battery equipped with the positive electrode which consists of the oxide or sulfide in which a dope and a \*\* dope of a lithium are possible, and the negative electrode which consists of carbonaceous material in which a dope and a \*\* dope of a lithium metal, a lithium alloy, or a lithium ion are possible and is suitable.

[0027] For example, when it constitutes a lithium secondary battery, as a positive active material, the metallic sulfide which does not contain the lithium of TiS2, MoS2, NbSe2, and V2O5 grade, an oxide, or the lithium multiple oxide containing a lithium can be used.

[0028] In order to constitute the cell which has high-energy density especially, the lithium multiple oxide which makes a subject LixMO2 (one or more kinds of transition metals of M are desirable, and it is 0.05<=x<=1.10 among a formula.) is used preferably. As a lithium multiple oxide, LiCoO2, LiNiO2, LixNiyCo1-yO2 (among a formula, x and y change with electric discharge states of a cell, and are usually 0< x<1 and 0.7< y<=1.), and LiMn2O4 grade are mentioned concretely.

[0029] According to composition of a request of the carbonate of a lithium, a nitrate, an oxide or a hydroxide, and carbonates, such as cobalt, manganese, or nickel, a nitrate, an oxide or a hydroxide, pulverization mixture of such a lithium multiple oxide can be carried out, and it can be adjusted by calcinating by the 600-1000-degree C temperature requirement in oxygen atmosphere.

[0030] Moreover, as a negative electrode, lithium alloys, such as a lithium and an Li-aluminum alloy, or the carbon material in which a dope and a \*\* dope of a lithium ion are possible can be used. What

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

#### **EXAMPLE**

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to this.

[0036] The concentration of lithium salt was changed into siloxane derivative (1) - (3) shown by \*\* 6 of the example 1 following --izing 8, and it added, respectively. And these were inserted into the stainless steel board of 2 the thickness of 0.145cm, and an area of 0.7854cm, respectively, and it asked for conductivity from the so-called Kohl Kohl (Cole-Cole) plot which expressed the sine-wave-alternating-current voltage to impress by the symbolic method (complex notation). This result is shown in Table 1.

[0037] In addition, the siloxane derivatives (3) in which the siloxane derivative (2) in which the siloxane derivative (1) in which the coefficient of kinematic viscosity in each 25 degrees C is shown by \*\* 6 is shown by 100cSt(s) and \*\* 7 is shown by 1600cSt(s) and \*\* 8 were 400cSt(s). [0038]

[Formula 6] 
$$CH_3$$
  $CH_3$   $CH$ 

・構造式(1)

[0040]  
[Formula 8]  

$$CH_3$$
  $CH_3$   $CH_3$ 

・・構造式(3)

[0041]
[Table 1]

Laurer				
サンプルNo.	シロキサン誘導体	Li塩の種類	重量モル濃度(m)	導電率(25℃)[mS・cm <sup>-1</sup> ]
サンプル1	構造式(1)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLi	0.5	2.20x10 <sup>-1</sup>
サンプル2	構造式(1)	(CF3SO2)2NLI	1.0	2.25×10 <sup>-1</sup>
サンプル3	構造式(1)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	0.5	1.20x10 <sup>-1</sup>
サンプル4	構造式(1)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	1.0	1.26×10 <sup>-1</sup>
サンプル5	構造式 (2)	(CF3SO2)2NLi	0.5	2.09×10 <sup>-2</sup>
サンブル6	構造式 (2)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLi	1.0	4.05×10 <sup>-2</sup>
サンプル7	構造式(2)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	0.5	3.64x10 <sup>-2</sup>
サンプル8	構造式 (2)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLI	1.0	3.80×10 <sup>-2</sup>
サンブル9	構造式(3)	(CF3SO2)2NLi	0.5	4.62×10 <sup>-2</sup>
サンブル10	構造式(3)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> NLi	1.0	4.80×10 <sup>-2</sup>
サンプル11	構造式 (3)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLi	0.5	2.75×10 <sup>-2</sup>
サンプル12	構造式 (3)	(CF <sub>3</sub> SO <sub>2</sub> ) <sub>3</sub> CLI	1.0	2.88×10 <sup>-2</sup>

[0042] The result of Table 1 shows that each siloxane derivative shown by \*\* 6 --izing 8 has the conductivity which can be used for a cell. Moreover, in siloxane derivative (1) - (3) from which a coefficient of kinematic viscosity differs, it turns out that conductivity with higher using the siloxane derivative (1) which has a low coefficient of kinematic viscosity more can be obtained.

[0043] The cyclic voltamogram of the siloxane derivative (1) shown by \*\* 6 and \*\* 7 of the example 2 point and (2) was measured, and oxidation stability was investigated. Measurement used the electrochemical cell made from three electrodes, and used the lithium metal for the operation pole on the nickel electrode (diameter: 0.5mm), the counter electrode, and the reference pole. And potential until the oxidation current of 100microA-cm -2 occurs was made into the range of stable potential. Consequently, 5.8V and the oxidization stable potential of a sample 6 were set to 6.0V by the oxidization stable potential of a sample 2.

[0044] This result shows that a siloxane derivative can demonstrate the cell performance which was excellent also in the high voltage.

[0045] The coin cell siloxane derivative [ which is shown to LiCoO2 and a negative electrode by the carbon material, and is shown in the electrolytic solution by \*\* 6 ] (1) Used for example 3 positive electrode was produced, and the charge and discharge test was performed. Upper-limit voltage: Charge and discharge were repeated up to 20 cycles on condition that 4.2V, minimum voltage:3.0V, and discharge current:100microA. The charge and discharge test at that time is shown in drawing 1 [0046] The result of drawing 1 shows that a siloxane derivative (1) has the cell performance which was excellent as a cell.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

# **DESCRIPTION OF DRAWINGS**

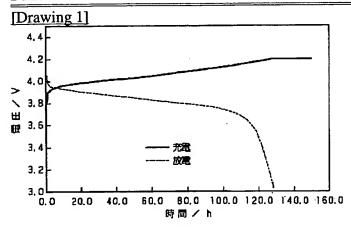
[Brief Description of the Drawings]

Drawing 1] It is the property view showing the charge-and-discharge curve of the nonaqueous electrolyte cell of this example.

Japan Patent Office is not responsible for any damages caused by the use of this translation.

- 1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

# **DRAWINGS**



シロキサン電池の充放電曲線

THIS PAGE BLANK (USPTO)